Polysiloxane Based Interpenetrating Polymer Networks: synthesis and Properties

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Abstract This article summarizes a large amount of work carried out in our laboratory on polysiloxane based Interpenetrating Polymer Networks (IPNs). First, a polydimethylsiloxane (PDMS) network has been combined with a cellulose acetate butyrate (CAB) network in order to improve its mechanical properties. Second, a PDMS network was combined with a fluorinated polymer network. Thanks to a perfect control of the respective rates of formation of each network it has been possible to avoid polymer phase separation during the IPN synthesis. Physicochemical analyses of these materials led to classify them as "true" IPNs according to Sperling's definition. In addition, synergy of the mechanical properties, on the one hand, and of the surface properties, on the other hand, was displayed.

1 Introduction

Interpenetrating polymer networks (IPNs) can be a smart solution in order to avoid some polymer defects. Indeed, these polymer associations generally lead to materials exhibiting better mechanical properties, increased resistance to degradation and a possibly improved combination of the properties of their components, i.e. a synergetic effect. All these characteristics come from the particular architecture of IPNs which combine two or more polymer networks synthesized in juxtaposition [1,2]. In addition, the entanglement of cross-linked polymers leads to forced "miscibility" compared to usual blends and the resulting materials exhibit a good dimensional stability over time. IPNs can be prepared through different synthetic pathways. In the *in situ* synthesis, all reactants are mixed together and the polymerization/cross-linking reactions leading to formations

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of the two networks can be started simultaneously or sequentially one after the other. Hence in this process, the reaction mechanisms must be of different nature, otherwise a single copolymer network instead of a true IPN is formed through cross reactions.

Although the final material is stable, a phase segregation occurring during the synthesis cannot be avoided. Qualitative information about the extent of phase separation in the IPN can be derived straight from the relative transparency of the material. Indeed, the more transparent the material, the smaller the phase separation, since any light wavelength will be diffracted by any phase domain the size of which is of the same order of magnitude, making the material appear translucent to opaque [1]. Dynamic Mechanical Thermal Analysis (DMTA) is also an adequate tool in order to corroborate the interpenetrating extent of both networks inside the IPN architecture. Ideally, interpenetration should occur only through physical interactions and the polymer network mixture should be homogeneous on a molecular scale without covalent bonding between the different networks. In this case, the DMTA analysis only detects one phase, witnessed by just one mechanical relaxation, the corresponding domain size being estimated at about 5–50 nm depending on the width of the relaxation signal [3]. Thus, this “single” phase is characterized through the loss factor (tanδ)-temperature curve by only one peak located at a temperature between those of the mechanical relaxation of the single networks combined inside the IPN architecture.

Siloxanes have a set of extremely interesting properties, i.e. very low surface energy, excellent gas and moisture permeability, good heat stability, low temperature flexibility and biocompatibility [4] but, because of weak intermolecular interactions between polymer chains, they exhibit also poor mechanical properties remaining a drawback for certain applications. Thus, low failure stress and low tear resistance limit silicone rubber applications in biomedical domain [5]. Besides, fluorine-containing elastomers maintaining rubber-like elasticity in extremely severe environments including exposure to high temperatures and corrosive chemicals have been developed. Fluorinated polysiloxane single networks have been prepared by sol-gel reaction or by hydrosilylation reaction and they are mainly used as protecting coatings. However the synthesis pathways leading to the telechelic precursors of those networks do not allow a fine control of the molar mass, polymolecularity and functionality. In addition, fluorinated polysiloxane networks do not show convenient mechanical properties at room temperature which restrains also their development. Thus, it can be interesting to elaborate a material combining a fluorinated polymer and a non fluorinated silicone independently.

Combining silicones with any organic polymer into a new material brings about some unique challenges. Indeed, polydimethylsiloxanes (PDMS) are known for their incompatibility with other polymers due to their low solubility parameter and extraordinary flexibility which makes them difficult to entrap into a polymer combination. Some IPNs associating PDMS with a thermoplastic polymer [6] such as PMAA [7], polyurethane [8], PMMA [9,10], polystyrene [11] or polycarbonate [12], have led to biphasic materials exhibiting higher mechanical properties than those of a single PDMS network.

The present work shows how it is possible to combine a PDMS network with two different partner polymer networks into IPN architecture in order to overcome some of PDMS weaknesses. Although these associations are not thermodynamically favored, a homogeneous material can be obtained by adjusting the relative formation rates of the two partner networks. Thus, first, a PDMS network was combined to a cellulose acetate butyrate (CAB) network in order to improve the PDMS thermomechanical properties. Second, PDMS was associated with a fluorinated network in order to find an alternative to the elaboration of materials keeping only the advantageous characteristics of fluorinated polysiloxane single networks. For each series the weight proportions of the two partner networks vary from gross 25 to 75 wt%. All IPNs presented here have been synthesized according to an *in situ* synthesis strategy and characterized by different techniques. Thus, new properties or the exaltation of one property were searched in order to know what could arise from the particular IPN architecture.

2 Experimental Section

α,ω-(3-hydroxypropyl)polydimethylsiloxane (diOH-PDMS oligomer – Mn_{NMR} = 1100 $g.mol^{-1}$) was kindly provided by Rhodia and was dried at least 3 days under vacuum (0.1 mmHg) before use. α,ω-divinyl polydimethylsiloxane (divinyl-PDMS oligomer-Mn_{NMR} = 650 $g.mol^{-1}$) and cellulose acetate butyrate (CAB – Mn = 16 000 $g.mol^{-1}$ – 4% acetate –50% butyrate –46% OH,) were purchased in ABCR and Acros Organics, respectively. The fluorinated acrylate (AcRf6) was synthesized as previously described [13].

Dibutyltindilaurate (DBTDL, Aldrich), ethylene glycol dimethacrylate (EGDMA, Aldrich), trimethylolpropane tris(3-mercaptopropionate) (Trithiol, Aldrich), and Desmodur® N3300 pluri-isocyanate cross-linker (Bayer) (NCO content: 21.8 ± 0.3 wt% according to the supplier) were used as received. This last compound is described as an isocyanurate mixture resulting from the condensation of three to several hexamethylene diisocyanate molecules and mainly composed of mono-, di- and tri-isocyanurates with a global functionality higher than 2 [14]. 2,2-azobis isobutyronitrile (AIBN, Acros Organics) was recristallized in methanol before use. Dicyclohexylperoxidicarbonate (DCPD, Groupe Arnaud) was dried under vacuum before use. Toluene (Carlo Erba, puro grade) and chloroform (Carlo Erba, puro grade) were distilled and dried before use.

PDMS-CAB IPNs were prepared by dissolving CAB in chloroform (5 mL per gram), then di-vinyl-PDMS, trithiol ([HS]/[C = C] = 1.1), Desmodur® N3300 ([NCO]/[OH] = 0.60), DBTDL ([DBTDL]/[OH] = 0.05), and AIBN ([AIBN]/[C = C] = 0.05) were added and the mixture was stirred under nitrogen atmosphere for 30 min. The mixture was then introduced in a mould made from two glass plates clamped together and sealed with a 1 mm thick Teflon® gasket. The mould was then kept at 50°C for 16 h. After 16 h, the sample was dried and post-cured for 2 h at 60°C.

PDMS/polyAcRf6 IPNs were synthesized by mixing together the appropriate weights of α,ω-(3-hydroxypropyl) polydimethylsiloxane (diOH-PDMS oligomer), Desmodur® N3300 pluri-isocyanate ([NCO]/[OH] = 1.2), DBTDL ([DBTDL]/[OH] = 0.014), AcRf6, EGDMA ([EGDMA]/[AcRf6] = 0.05) and DCPD

([DCPD]/[C = C] = 0.05) in 2 mL toluene under argon. Then, the mixture was introduced into a mould. The mould was heated in an oven at 55°C for 15 h. Toluene was then taken off under vacuum.

For all the IPNs, the same proportions between monomer, cross-linker and catalyst or initiator in a same network were kept whatever the IPN composition.

The soluble amounts contained in the final materials were determined by Soxhlet extraction with an adequate solvent and the weight percentages were calculated as $EC(\%) = (W_0 - W_E)/W_0 \times 100$ where W_0 and W_E are the weights of samples before and after extraction respectively.

DMTA measurements were carried out on film samples with a Q800 apparatus (TA Instruments) operating in tension mode. Experiments were performed at a 1 Hz frequency and a heating rate of 3°C min^{-1} from –120 to 100°C.

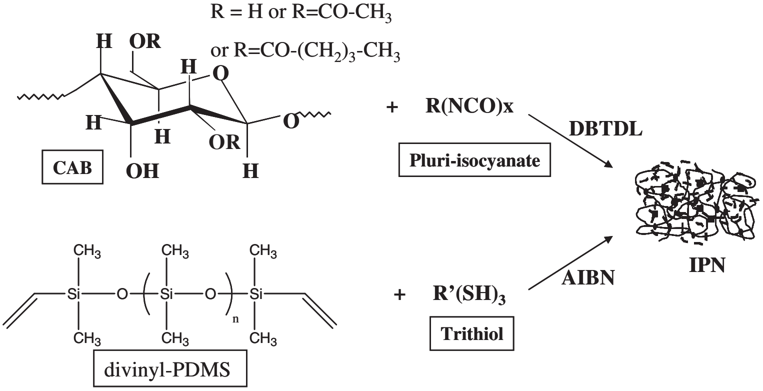
The liquid-film contact angles (θ) were determined from image recordings by video microscopy after deposition of a 25 μL water drop at 20°C on the material surfaces. For these measurements, the samples, synthesized between two glass plates, were unmoulded and hung in air without contact with any material during drying. The values of equilibrium contact angles were computed after processing the images with a frame grabbing software (Drope Shape Analysis). For each composition, contact angles were measured on about six samples resulting from different syntheses; four drops per sample were analyzed. The reported contact angle values correspond to the average of all measurements with an error bar corresponding to twice the standard deviation.

3 Results and Discussion

All IPNs presented here have been synthesized according to an *in situ* synthesis strategy, i.e. all network precursors were mixed together in a suitable solvent in order to obtain a homogeneous starting solution. By choosing this IPN synthesis pathway, it is important to check that no side reaction occurs during the synthesis. For both series and throughout the studied weight composition range, it was checked that soluble fraction contained in IPNs was lower than 10 wt% which is characteristic of a satisfactory cross-linking degree of the networks inside the IPNs.

3.1 PDMS/CAB IPN

First, PDMS network was combined to a cellulose acetate butyrate (CAB) network into an IPN architecture in order to improve the thermomechanical properties of PDMS network (Scheme 1). The linear CAB can be cross-linked through its free OH groups with a Desmodur® N3300 pluri-isocyanate. The alcohol/isocyanate reaction is catalyzed by DBTDL leading to urethane cross-links. Simultaneously, PDMS oligomers must be cross-linked independently in order to form the PDMS network. In order to carry out independent cross-linking reactions, divinyl-PDMS has been chosen as the PDMS precursor. This oligomer does not react according to a free-radical thermal initiated polymerization. Thus this possibility was discarded and a thiol-ene addition cross-linking was considered instead. The silicone network was formed through a thiol-ene addition initiated with AIBN between α,ω-divinyl-polydimethylsiloxane and trimethylolpropane tris(3-mercaptopropionate) (trithiol) as a cross-linking agent.



Scheme 1 Synthesis pathway of PDMS/CAB IPNs

Previous kinetic studies [15] have shown that thiol functions from the divinyl-PDMS cross-linker do not react with isocyanate groups from the CAB cross-linker and that the obtained IPNs are not grafted. However, thiol groups form stable species with the DBTDL catalyst which in turn results in decreasing the actual available quantity of catalyst in the medium thus slowing down the CAB network formation. Consequently, in order to obtain a transparent material withstanding the presence of thiol functions the DBTDL proportion must be increased. Indeed, it was shown that the NCO conversion level must be at least 40% before the complete PDMS network formation in order to avoid phase segregation. Thus, the exact DBTDL amount has been determined for each PDMS/CAB weight proportion in order to obtain a transparent IPN which is characteristic of the absence of phase separation during the synthesis.

The absence of phase segregation has been confirmed by DMTA measurements. Indeed, PDMS/CAB IPNs show only one mechanical relaxation lying between those of the single CAB and PDMS networks (Fig. 1).

These results show that the networks are correctly interpenetrated and no phase separation is observed at the DMTA level. Thus, these IPNs exhibit many characteristics, which would allow considering them as close to "true" IPNs.

In order to check whether the mechanical properties of the PDMS network are really improved by the CAB network introduction in a final IPN material, the stress-strain curves of PDMS/CAB IPNs with different compositions were recorded (Fig. 2). The PDMS and CAB single networks break when less than 10 and 5% strains are applied respectively. On the other hand, the elongation at break is over 150% for the PDMS/CAB (50/50) IPN. Thus, the poor mechanical properties of the PDMS

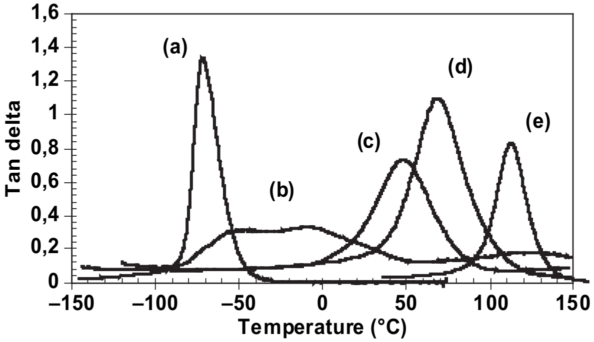


Fig. 1 tanδ versus temperature of PDMS/CAB IPNs with different weight compositions (b) 75/25, (c) 50/50 and (d) 25/75. PDMS (a) and CAB (e) single network curves are reported for comparison.[16]

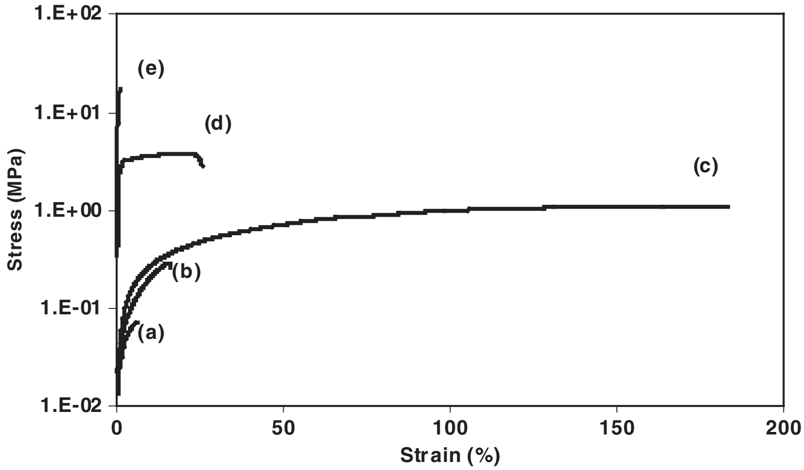
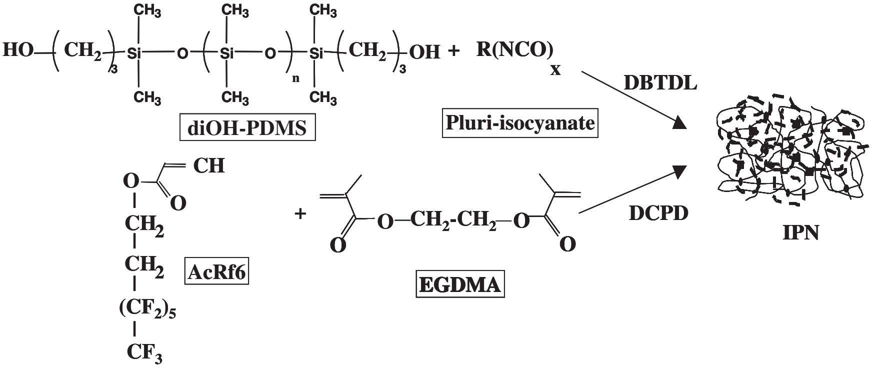


Fig. 2 Stress-strain curves of PDMS (a) and CAB (e) single networks and of PDMS/CAB IPNs with different compositions (b) 75/25, (c) 50/50 and (d) 25/75. Deformation rate: 1 mm.min^{-1} – T = 35°C.[16]

network are clearly and significantly reinforced by combining it into an IPN with 50 wt% CAB, for example. This stress-strain behaviour is indicative of a synergistic effect involving the elongation at break and arising from the IPN architecture. For other IPN compositions, the extent of this synergetic effect is limited but still exists.

3.2 PDMS/polyAcRf6 IPN

The fluorinated network has been elaborated starting from 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (AcRf6) by free-radical co-polymerization with ethylene glycol dimethacrylate in the presence of DCPD as the initiator. In this case, the PDMS network could not be synthesized by thiol-ene addition otherwise a co-network would have been obtained. Thus PDMS network was formed starting from α,ω-(3-hydroxypropyl)polydimethylsiloxane (diOH-PDMS oligomer) by DBTDL catalyzed addition between the hydroxy end groups and an pluri-isocyanate cross-linker (Scheme 2). No side reaction has been detected between these precursors.



Scheme 2 Synthesis pathway of PDMS/polyAcRf6 IPNs

The extent of network interpenetration in these IPNs has been shown by different techniques and studied as a function of PDMS/polyAcRf6 composition [13]. As previously shown, DSC and DMTA are suitable techniques to detect the occurrence of phase separation in IPNs. Here, DSC and DMTA measurements show only one glass transition and only one broad mechanical relaxation, respectively, the positions of which depend on the IPN composition. However, the fact that the Tg values of the two single networks are close to each other (Tg(PDMS) = −25°C and Tg(polyAcRf6) = +3°C) can explain why only one broad transition is observed in the different IPNs. For this reason, other techniques have been used in order to obtain more information about the interpenetration degree of the two partner networks. Thus, for all IPN compositions the specific volumes are higher than the values of the linear combination of those of the single networks and this behavior cannot be matched with that of a blend in which polymers are not miscible. In other words, PDMS/polyAcRf6 IPNs possess densities lower than those predicted by additive volume law: that suggests the presence of repulsion forces between partner networks. This is in agreement with the known incompatibility of fluorinated compounds with non-fluorinated ones. However, those repulsions have been overcome by the counteracting cross-linking effect since no macroscopic phase separation is observed (IPNs are transparent). These results have been also confirmed by measurements of IPN refractive indices and their comparison with those calculated from Lorentz-Lorentz equation.

Finally, the hydrophobic character of a polymeric material can be estimated from contact angle measurements of a water drop deposited on its surface, the values of the contact angle depending on the chemical composition of the surface. Fluorinated polymers having good hydrophobic and oleophobic properties and silicones being hydrophobic as well, the contact angles measured on PDMS/polyAcRf6 IPNs should be larger than 90°. The association of two networks in IPN architecture can lead to a material the properties of which correspond to a value in between those of the two single partner networks. The contact angle of water drop deposited on PDMS/polyAcRf6 IPN surface has been measured as a function of polyAcRf6 weight proportion (Fig. 3). Remarkably, the combination of the fluorinated and PDMS networks into an IPN architecture leads to a linear increase of the contact angle from 114 to 123° for single PDMS network to PDMS/polyAcRf6 (25–75) IPN respectively. For polyAcRf6 contents higher than 75 wt%, the contact angle sharply decreases down to 117°, which corresponds to the angle measured on the polyAcRf6 single network surface. Thus the contact angle is maximum for the PDMS/polyAcRf6 (25/75) IPN and contrary to what is generally observed on copolymer surfaces [17], the contact angle does not vary monotonously with the polyAcRf6 weight proportion.

In order to check that this phenomenon is intrinsic to the material and does not result for example from the migration of unreacted starting materials towards the surface, contact angles have been measured on the surface of the same IPNs before and after extraction in a Soxhlet (Fig. 3). Contact angles remain unchanged after this treatment i.e. the observed phenomenon is specific to those IPNs. The high contact angle values of fluorinated compounds are due to the surface concentration of CF_3 groups. The above IPN density measurements have shown that repulsive interactions are established in IPNs between PDMS and polyAcRf6 networks, resulting in a volume expansion of the material. During the IPN synthesis, the fluorinated grafts probably reorganize so as to minimize those repulsions and can in particular concentrate at the surface. Thus the surface concentration of the fluorinated grafts could as a result be higher in the IPNs than in the single network leading to an interesting synergy of the surface properties.

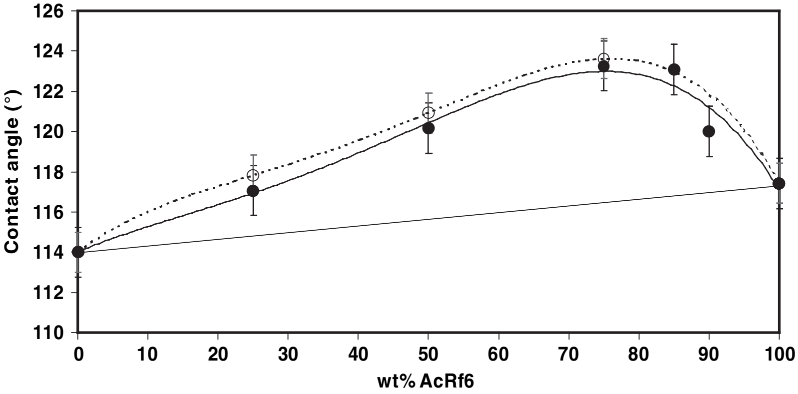


Fig. 3 Water contact angles of the surface of PDMS/polyAcRf6 IPNs vs polyAcRf6 weight proportion measured on IPNs before (●) and after (○) Soxhlet extraction with F113 for 48 hours.[13]

4 Conclusion

These results summarize a large amount of work carried out in our laboratory on polysiloxane based Interpenetrating Polymer Networks (IPNs). First, a polydimethylsiloxane (PDMS) network has been combined with a cellulose acetate butyrate (CAB) network in order to improve its mechanical properties. Thanks to a perfect control of the respective formation rates of networks it has been possible to avoid polymer phase separation during the IPN synthesis. Indeed, PDMS/CAB IPNs are transparent and only one mechanical relaxation was detected by DMTA measurements which are characteristic of "true" IPNs. In addition, a synergy effect is observed on the stress-deformation curves. Second, a PDMS network was combined with a fluorinated polymer network and the resulting IPNs can also be considered as "true" IPNs. In this case, a synergy of the surface properties was displayed.

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